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## METASTABLE PHASE RELATIONSHIPS IN THE SYSTEM

$\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$

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*The diagram of metastable phase relationships of the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$  which occur as a result of the metastable behavior of the compound  $\text{Y}_3\text{Al}_5\text{O}_{12}$  is plotted. This diagram differs from the equilibrium ternary diagram by the absence of  $\text{Y}_3\text{Al}_5\text{O}_{12}$  and corresponding changes in solidification processes for the ternary system.*

The system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$  is fundamental in the material science of high technology ceramics. On the basis of this system a ceramic with a strength of 2400 MPa and fracture toughness of the order of  $10 \text{ MPa}\cdot\text{m}^{1/2}$  has been obtained. Depending on their composition different mechanisms for improving strength and toughness are realized in materials: transformation (ceramics based on  $\text{ZrO}_2$ ), dispersion strengthening (materials based on  $\text{Al}_2\text{O}_3$ ), fiber reinforcement (directionally solidified eutectics  $\text{Al}_2\text{O}_3 - \text{ZrO}_2(\text{Y}_2\text{O}_3)$ ,  $\text{Al}_2\text{O}_3 - \text{Y}_3\text{Al}_5\text{O}_{12}$ ), etc. Materials based on  $\text{ZrO}_2$  are used for preparing high-temperature windows which are stable in corrosive atmospheres and transparent in the visible and near (about  $2 \mu\text{m}$ ) IR-regions of the spectrum.

The constitution diagram for the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$  has been studied quite completely [1-4]. However in the binary restricted system  $\text{Al}_2\text{O}_3 - \text{Y}_2\text{O}_3$  in the composition range 50-100% (mol.)  $\text{Al}_2\text{O}_3$  (A) Caslavsky and Viechnicki [5] detected metastable states connect with the ambiguous behavior of the compound  $\text{Y}_3\text{Al}_5\text{O}_{12}$  ( $\text{Y}_3\text{A}_5$ ) on melting. It is shown in [6-9] that after superheating by about 100 degrees the melt in the range for existence of  $\text{Y}_3\text{A}_5$  and subsequent solidification ingots do not contain  $\text{Y}_3\text{A}_5$  but a mixture of primary crystals of  $\text{YAlO}_3$  (YA) and eutectic  $\text{YA} + \text{Al}_2\text{O}_3$ . This behavior of  $\text{Y}_3\text{A}_5$  is explained by the fact that in the liquid with increasing temperature heterophase complexes of  $\text{Y}_3\text{A}_5$  with a coordination number (CN) for aluminum of four break down. An increase in the CN for aluminum to six is more suitable from an energy point of view at high temperature and it corresponds to the CN for aluminum in the compound YA. As a result of this a mixture of  $\text{YA} + \text{Al}_2\text{O}_3$  solidifies instead of  $\text{Y}_3\text{A}_5 + \text{Al}_2\text{O}_3$  [5, 7, 8].

The aim of the present work is to construct a diagram for metastable phase relationships in the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$  for which there are no published data, and also to clarify the diagram for metastable relationships in the system  $\text{Al}_2\text{O}_3 - \text{Y}_2\text{O}_3$ .

The starting powders were analytical grade  $\text{Al}_2\text{O}_3$  (TU 6-09-426-75), pure grade  $\text{ZrO}_2$  (TU 6-09-2486-77) produced by the Donetsk Chemical Reagent Plant, and  $\text{Y}_2\text{O}_3$  grade ITO-Lyum prepared at the Physicochemical Institute of the Ukrainian National Academy of Sciences (Odessa). Specimens were prepared by grinding the powders in an agate mortar in a medium of ethanol followed by pressing in the form of tablets 5 mm in diameter and thick with a stepwise change (through 5% (mol.)) in the concentration of the components. Heat treatment was performed in helium using a device for DTA. The crucible material was molybdenum. Specimens were studied by DTA up to  $2500^\circ\text{C}$  [10], derivative thermal analysis in air ( $\sim 3000^\circ\text{C}$ ) using a solar device [11] accurate to within  $\pm 20^\circ\text{C}$ , x ray (DRON-1.5,  $\text{CuK}_\alpha$ -radiation, Ni-filter), petrographic (MIN-8), and microstructural (MIN-7, Camebax SX-50) phase analyses. Microsections were prepared by grinding on diamond disks followed by polishing on diamond pastes of different size fractions. In order to realize metastable phase relationships a melt was superheated by 50-100 degrees above the liquids temperature and solidified at a rate not exceeding 5 deg/min.

The constitution diagram is presented in Fig. 1 for the system  $\text{Al}_2\text{O}_3 - \text{Y}_2\text{O}_3$  in the composition range 50-100% (mol.)  $\text{Al}_2\text{O}_3$  plotted using data in [5-9, 12-14] and the results of the present study. The broken lines show the metastable phase

TABLE 1. Coordinates for Invariant Points of the Diagram for Metastable Phase Relationships of the System  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$

Invariant points	Temperature, °C	Liquid phase composition, % (mol.)			Invariant reactions
		$\text{Al}_2\text{O}_3$	$\text{ZrO}_2$	$\text{Y}_2\text{O}_3$	
$E_1$	1910	26	6	68	liquid $E_1 = \text{Y}_2\text{A} + \text{F} + \text{C}$
$E_2$	1850	37	10	53	liquid $E_2 = \text{YA} + \text{F} + \text{Y}_2\text{A}$
$P$	1745	63	25	12	liquid $P + \text{T} = \text{F} + \text{A}$
$E'_3$	1650	67	12	21	liquid $E'_3 = \text{A} + \text{F} + \text{YA}$

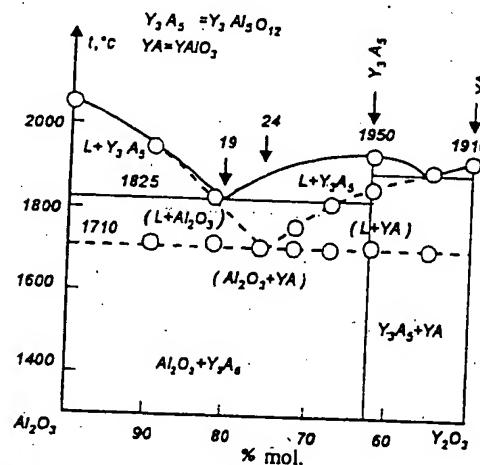


Fig. 1. Constitution diagram for the system  $\text{Al}_2\text{O}_3 - \text{Y}_2\text{O}_3$ .  
Points are data from the present work.

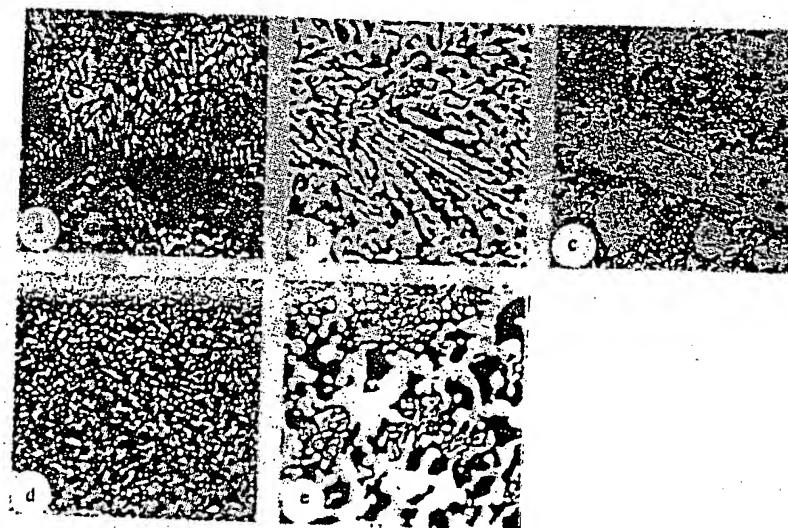


Fig. 2. Microstructure of some alloys of the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$  solidified in different schedules.

relationships in this system expressed in the formation of the simple eutectics system  $\text{Al}_2\text{O}_3 - \text{YA}$  with coordinates of the eutectic  $1710^\circ\text{C}$  and 76% (mol.)  $\text{Al}_2\text{O}_3$  which is good agreement with data in [5, 6]. The microstructure of this metastable eutectic is given in Fig. 2a.

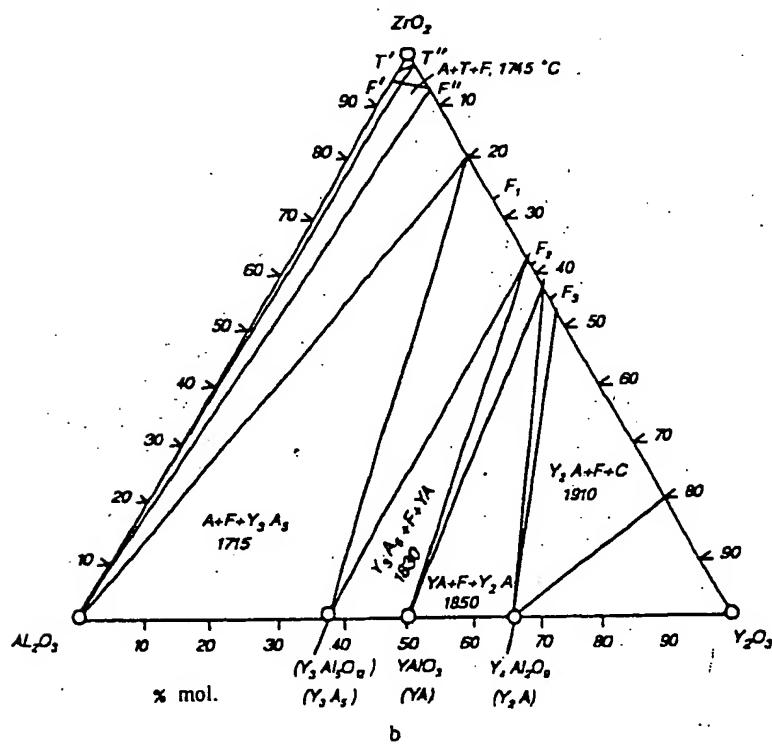
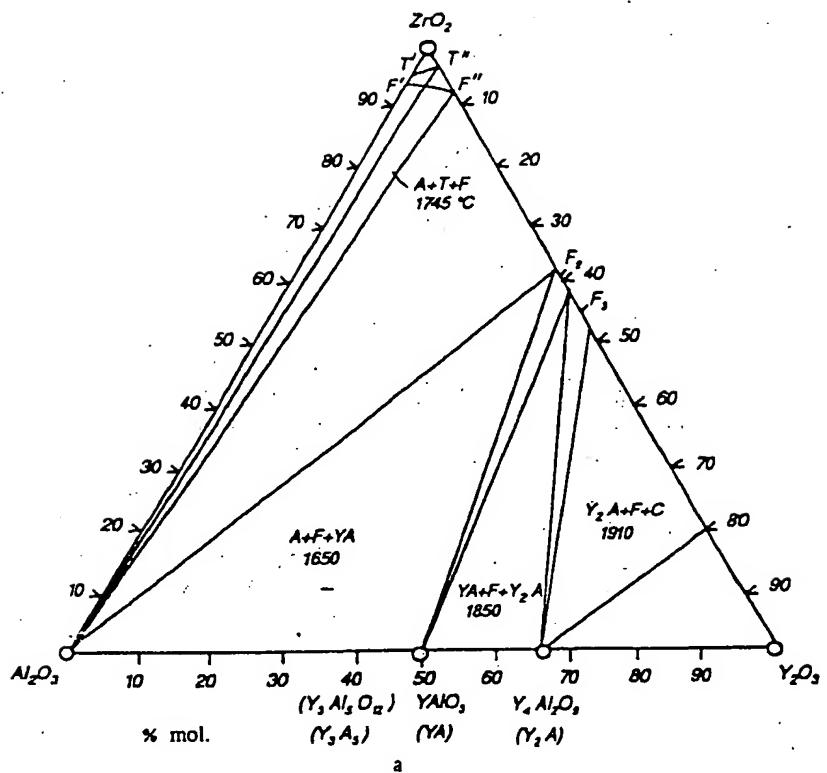


Fig. 3. Projection of the solidus surface for the system  $\text{Al}_2\text{O}_3$ – $\text{ZrO}_2$ – $\text{Y}_2\text{O}_3$ : Here and in Fig. 4: a) metastable phase relationship diagram; b) constitution diagram.

In the system  $\text{Al}_2\text{O}_3$ – $\text{ZrO}_2$ – $\text{Y}_2\text{O}_3$  only the phase  $\text{Y}_3\text{A}_5$  exhibits metastable properties and therefore the diagram for phase relationships in the secondary system  $\text{YA}$ – $\text{F}_2$ – $\text{Y}_2\text{O}_3$  (Fig. 3a, b), where  $\text{F}_2$  is a solid solution of the composition 61% (mol.)  $\text{ZrO}_2$ –39% (mol.)  $\text{Y}_2\text{O}_3$  [1], does not differ from the composition diagram for the same part of the system  $\text{Al}_2\text{O}_3$ – $\text{ZrO}_2$ – $\text{Y}_2\text{O}_3$  [1-4]. The metastability for  $\text{Y}_3\text{A}_5$  only appears in part of the system bounded by the quads angle  $\text{Al}_2\text{O}_3$ – $\text{ZrO}_2$ – $\text{F}_2$ – $\text{YA}$ . Melting of specimens whose composition is within this quads angle showed that they only contain

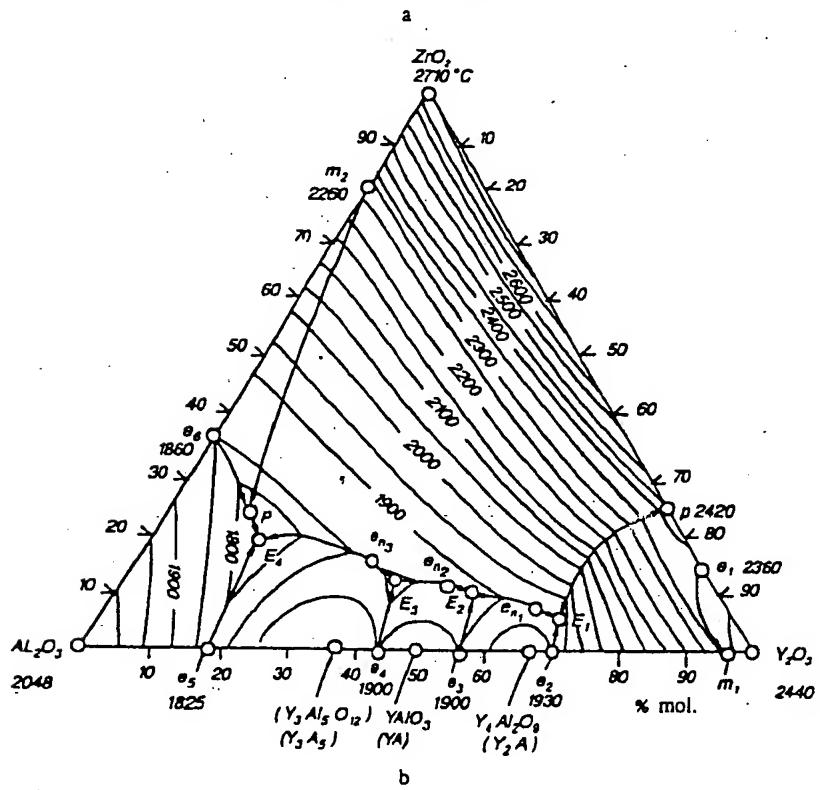
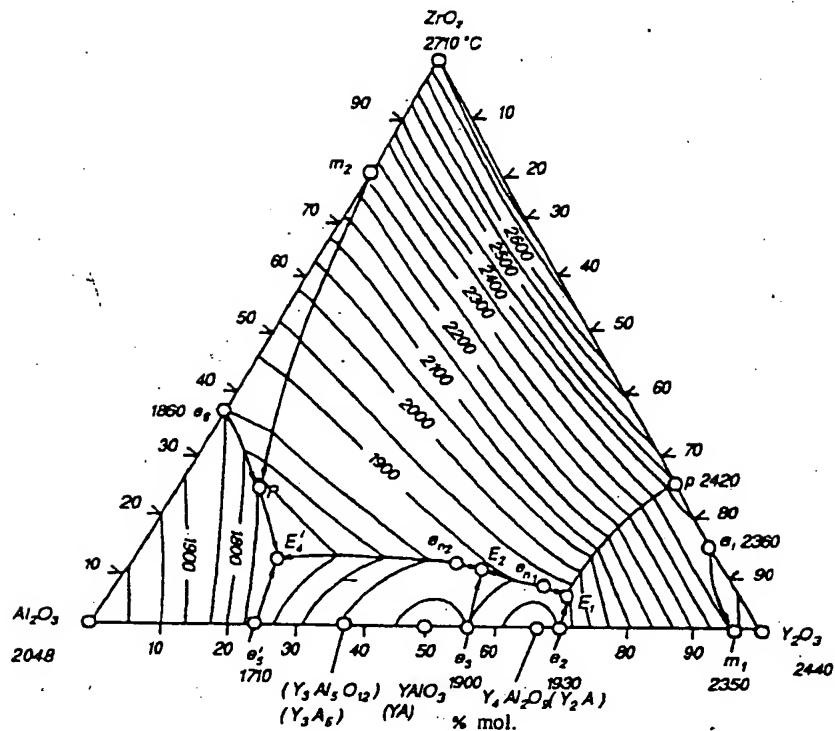


Fig. 4. Projection of the liquidus surfaces for the system  $\text{Al}_2\text{O}_3$ – $\text{ZrO}_2$ – $\text{Y}_2\text{O}_3$ .

$\text{Al}_2\text{O}_3$ , YA, and solid solutions based on  $\text{ZrO}_2$  either with a tetragonal (T) or cubic structure of the fluorite type (F) depending on the  $\text{Y}_2\text{O}_3$  content.

Presented in Fig. 4a is a projection of the liquidus surface for the metastable phase relationship diagram of the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$ , and shown in Fig. 4b for comparison is a projection of the liquidus surface for the constitution diagram of this system studied previously [2]. The difference between the two diagrams is the absence from Fig. 4a of the primary solidification field for the  $\text{Y}_3\text{A}_5$  phase and as a result of this expansion of the primary solidification field for solid solution F

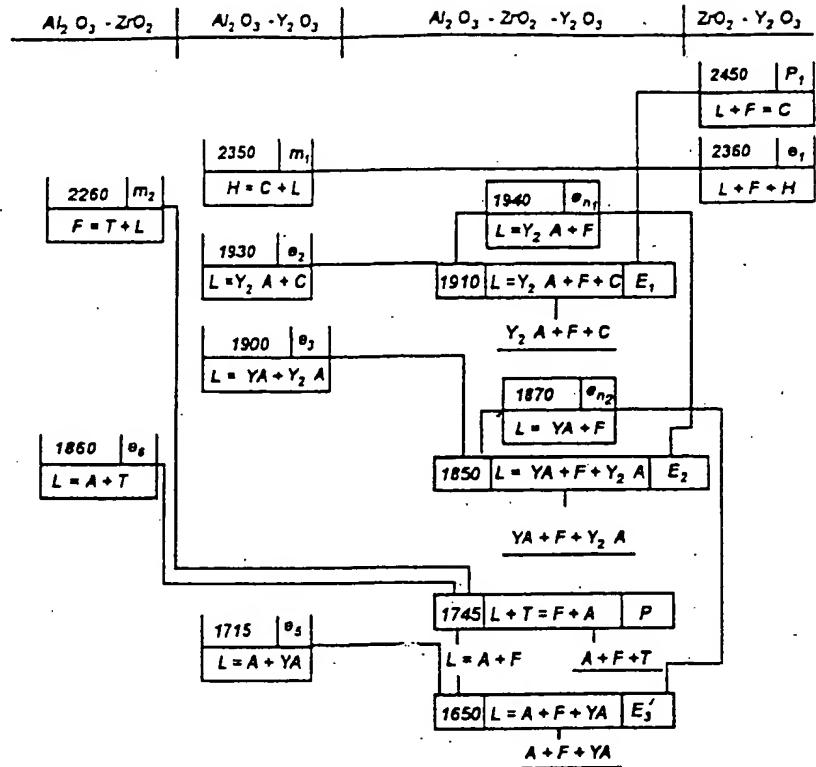


Fig. 5. Diagram of reactions which proceed with metastable solidification of specimens of the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$ .

and the phase YA. In addition there is no ternary eutectic point  $E_3$ , quasibinary eutectic point  $e_n$ , but a ternary eutectic point  $E'_3$  appears at which liquid coexists with  $\text{Al}_2\text{O}_3$ , F, and YA. Therefore the liquidus surface of the diagram for metastable phase relationships of the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$  is characterized by the presence of four four-phase invariant reactions of which three relate to a eutectic type, and one relates to a peritectic type, and two three phase invariant reactions (quasibinary eutectics):  $\text{YA} + \text{F}_2$  and  $\text{Y}_4\text{Al}_2\text{O}_9(\text{Y}_2\text{A}) + \text{F}_3$ , where  $\text{F}_3$  is solid solution of the composition 57% (mol.)  $\text{ZrO}_2$  - 43% (mol.)  $\text{Y}_2\text{O}_3$  [1]. The coordinates for invariant points of the diagram for metastable phase relationships of the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$  are given in Table 1.

Thus, the liquidus surface of the diagram for metastable phase relationships of the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$  is formed by seven fields of primary solidification of phases: T- and F-solid solutions based on  $\text{ZrO}_2$ , H- and C-solid solutions based on  $\text{Y}_2\text{O}_3$ ,  $\text{Y}_2\text{A}$ , YA and  $\text{Al}_2\text{O}_3$ . The main area of the liquids surface occupies the field of primary solidification for F-solid solutions bounded by the envelope  $m_2\text{P}E_3e_{n_2}E_2e_{n_1}E_1\text{P}$ , which points to high thermodynamic stability for this phase. The surface of primary solidification F intersects with similar fields for other phases along a curve for binary solidification of the corresponding eutectics. Solid solution F coexists with seven phases of the system, in addition to C-solid solution, and it reacts with them by a eutectic mechanism. An exception is the peritectic reaction  $\text{Li}_p + \text{T} = \text{F} + \text{Al}_2\text{O}_3$  which precedes metatetic  $\text{F} = \text{T} + \text{Li}$  and eutectic  $\text{L} = \text{A} + \text{T}$  reactions. The microstructure is shown in Fig. 2b, c of alloys of the same composition solidified respectively in metastable and stable regimes. In the first case this microstructure is a metastable ternary eutectic  $E'_3$ , and in the second it is primary crystals of  $\text{Y}_3\text{A}_5$  and ternary stable eutectic  $E_4$ . The microstructure is also presented for alloys of composition  $E_4$  solidified in different regimes (Fig. 2d, e). Coarse crystals of binary precipitate  $\text{Al}_2\text{O}_3 + \text{F}$  and fine ternary eutectic  $\text{Al}_2\text{O}_3 + \text{F} + \text{YA}$  ( $E_3'$ ) indicate (Fig. 2e) that this alloy solidified by a metastable regime falls on a monovariant curve of binary solidification  $\text{PE}_3'$  along which there is joint solidification of  $\text{Al}_2\text{O}_3$  and F-solid solutions.

In Fig. 3a there is a projection of the solidus surface for the diagram of metastable phase relationships of the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$ , and for comparison in Fig. 3b there is a projection of the solidus surface for the constitution diagram of this system [3]. Metastable behavior of  $\text{Y}_3\text{A}_5$  leads to the situation that there is a marked (compared with the equilibrium condition) increase in the linear surface for the end of solidification of binary eutectic  $\text{Al}_2\text{O}_3 + \text{F}$  (F-solid solution containing from 7 to 37% (mol.)  $\text{Y}_2\text{O}_3$ ) isothermal three-phase fields  $\text{Al}_2\text{O}_3 + \text{F} + \text{Y}_3\text{A}_5$ ,  $\text{Y}_3\text{A}_5 + \text{F} + \text{YA}$  are absent and isothermal three-phase  $\text{Al}_2\text{O}_3 + \text{F} + \text{YA}$  appears instead of them. Therefore the solidus surface for the diagram of metastable phase

relationships of the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$  consists of four isothermal three-phase fields relating to three invariant reactions of the eutectic type ( $\text{Li}_{E1} = \text{Y}_2\text{A} + \text{F} + \text{YA}$ ,  $\text{Li}_{E3} = \text{Al}_2\text{O}_3 + \text{F} + \text{YA}$ , where C is solid solution based on  $\text{C}-\text{Y}_2\text{O}_3$  with a different content of  $\text{ZrO}_2$ ) and one field of the peritectic type ( $\text{Li}_p + \text{T} = \text{F} + \text{Al}_2\text{O}_3$ ), linear surfaces of the region for the end of solidification of binary eutectics  $\text{Al}_2\text{O}_3 + \text{T}$ ,  $\text{Al}_2\text{O}_3 + \text{F}$ ,  $\text{YA} + \text{F}_2$ ,  $\text{Y}_2\text{A} + \text{F}_3$  and  $\text{Y}_2\text{A} + \text{C}$ , and also a linear surface  $\text{F}'\text{T}'\text{T}''\text{F}''$  formed by the sides of tie-line triangles which bear against equilibrium phases  $\text{T}$  and  $\text{F}$  (their compositions lie close to the  $\text{ZrO}_2$  apex) and move along the curves  $\text{T}'\text{T}''$  and  $\text{F}'\text{F}''$ .

Metastable solidification of alloys of the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$  is characterized (Fig. 5) four four-phase invariant transformations, and in fact: at 1910 ( $E_1$ ), 1850 ( $E_2$ ), 1745 ( $P$ ) and 1650°C ( $E_3'$ ). As also in the case of equilibrium solidification [3] and three-phase reaction, characterizing the metatectic process  $\text{F} = \text{T} + \text{Li}$ , occurs along a boundary curve  $m_2\text{P}$  with a reduction in temperature from 2260 to 1745°C and it is preceded by a four-phase invariant reaction  $\text{Li}_p + \text{T} = \text{F} + \text{A}$  at the temperature indicated. Then a monovariant process following peritectic reaction  $P$  occurs with a reduction in temperature along boundary curve  $\text{PE}_3'$  and it is also congruent in nature ( $\text{Li} = \text{F} + \text{A}$ ). Point  $E_3'$  corresponds to the composition of liquid participating in the four-phase invariant reaction  $\text{Li}_{E3} = \text{Al}_2\text{O}_3 + \text{F} + \text{YA}$  at 1650°C. At this point two more three-phase congruent processes cease:  $\text{Li} = \text{A} + \text{YA}$  and  $\text{Li} = \text{YA} + \text{F}$ .

Thus, the differences of the diagram for metastable phase relationships of the system  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Y}_2\text{O}_3$  which arise due to metastable behavior of the compound  $\text{Y}_3\text{Al}_5\text{O}_{12}$  with solidification from superheated melts from the constitution diagram for this system is the absence of the compound in the binary system  $\text{Al}_2\text{O}_3 - \text{Y}_2\text{O}_3$  and corresponding changes in solidification processes for the ternary system.

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